

Magnetism in Carbon Structures[★]

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Abstract

We discuss different magnetic phenomena observed in carbon-based structures, in particular the diamagnetism, paramagnetism and ferromagnetism observed in graphite, disordered carbon, fullerenes and irradiated carbon structures.

Key words: Magnetic carbon, Soft magnetic materials, Ferromagnetic semiconductors, Radiation effects

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1. Introduction

Within the fundamentals of magnetism we read in textbooks that the magnetic order in solids below a critical temperature, like ferro-, ferri- or antiferromagnetism, is characterized by a microscopic arrangement of atomic magnetic moments. In order to account for ferromagnetism one needs, for example, an exchange interaction of electrostatic origin between localized magnetic moments of neighboring atoms or, in case of itinerant electron magnetism, an effective exchange energy for the unpaired, no longer localized electrons. Within these basic, well accepted concepts, magnetic order was “recognized” only for materials with $3d$ or $4f$ electrons. However, since 1991 we know that some organic molecules with unpaired π -electrons show magnetic order at temperatures $T < 20$ K, without having any metallic ions [1]. We note also that antiferromagnetic order in a s, p -electron system has been found below a Néel temperature of ~ 50 K [2]. We are not aware of any law of physics that prohibits the existence of magnetic order in systems with only s, p -electrons and at temperatures above room temperature.

Not long time ago, carbon-based structures were basically accepted to be diamagnetic or, in special cases, paramagnetic. Any ferromagnetic-like signal was assumed to be due to magnetic impurities. No doubt, im-

purities are a problem when the “intrinsic” magnetic signals are relatively small. However, it appears that instead of trying to study systematically the contribution of these impurities to the magnetic signals, the strategy of “minimum work” based on prejudices was chosen, indirectly neglecting the existence of interesting magnetic phenomena in carbon structures. In this article we will review some recently published results that indicate that we are at the beginning of our understanding of the magnetism in carbon-based materials.

2. Diamagnetism in oriented graphite

Usually, a diamagnetic signal is measured in relatively ordered carbon-based structures. The best example is oriented graphite, which shows a large diamagnetic susceptibility. Measurements of highly oriented pyrolytic graphite samples with rocking curve width at half maximum FWHM $\leq 0.4^\circ$ provide a value for the susceptibility $\chi_{||} = -(2.4 \pm 0.1) \times 10^{-5} \text{ emu/gOe}$ at 300 K and for fields applied parallel to the c -axis (perpendicular to the graphene planes). The large diamagnetism stems from “fast-moving” electrons [3] with a small effective mass $m^* \sim 0.05m_0$ (here m_0 is the free electron mass). Within a tight-binding picture the small effective mass is due to the large π -bonding overlap of the neighboring C-atoms in a single layer given by the band parameter $\gamma_0 \propto 1/m^*$. For the calculation of χ the linear dispersion relation for two-dimensional (2D) graphene $E(k) \propto k$ was assumed [4]. On the other hand, properties of massless “Dirac” fermions are rediscovered nowadays in the literature and are thought to play also a role in the observed metal-insulator-like transition in the electrical resistivity [5]. The main contribution to the T -dependence of $\chi(T)$ at $T \gtrsim 150$ K is given by $\partial f / \partial E|_{E=E_F}$ (f is the Fermi-Dirac distri-

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bution function) due to the condensation of fermions into the Landau level with $n = 0$ after the application of a magnetic field [3]. Although experimental results are in general in agreement with this theory, to explain the saturation of $\chi(T)$ at low T a series of additional band parameters has to be included (see [6] and Refs. therein). We note, however, that this further developed theory does not account for the measured anisotropy of the g -factors [6], a disagreement that, to our knowledge, has not been solved yet. Moreover, high resolution magnetization measurements in different HOPG samples indicate that χ has a shallow but well-defined and field dependent minimum at $T \lesssim 30$ K (as an example see Fig. 1) in agreement with that reported in [7]. This minimum is not due to magnetic impurities. The origin for this minimum is not yet clarified and no attempt has been done to check whether it is compatible with more elaborate theories for the diamagnetism in graphite.

Due to the available sample quality, the measurement of the anisotropy in the carrier diamagnetism of graphite is difficult. Taking into account recent measurements of the electrical anisotropy that indicates a ratio (parallel to perpendicular to the c -axis) of the order of or larger than 10^4 for well ordered samples, we expect to have a susceptibility $|\chi_{\perp}|$ smaller than the atomic susceptibility of carbon in graphite, which is of the order of -5×10^{-7} emu/gOe according to literature. We have also to take internal misalignments of the crystallites in the sample into account. At room temperature and for a sample with FWHM $= 0.4^\circ$, due to the χ_{\parallel} component a value of the order of -1.7×10^{-7} emu/gOe $\ll \chi_{\perp}$ would be measured for fields applied nominally parallel to the planes. The effect of this internal misalignment has been verified by electrical conductivity measurements [8].

3. Paramagnetism in disordered carbon

If we increase the disorder in a graphite structure the main diamagnetic signal decreases in absolute value and turns to paramagnetic when the disorder is large enough. A clear example can be seen in Fig. 1 where the temperature dependence of the magnetization of a target made of an ultra-pure graphite powder [9] and of the material obtained from disordered carbon films prepared by pulsed laser deposition (PLD) on Si substrates [10] are shown. Due to the random alignment of the graphite crystallites in the graphite target, its diamagnetic susceptibility at 300 K is a factor three smaller than χ_{\parallel} for HOPG. The data for the disordered carbon material indicate a Curie-like dependence added to a Pauli-like contribution. The inset in Fig. 1 shows the field dependence of the magnetization for the carbon film material at 5 K. These data can be de-

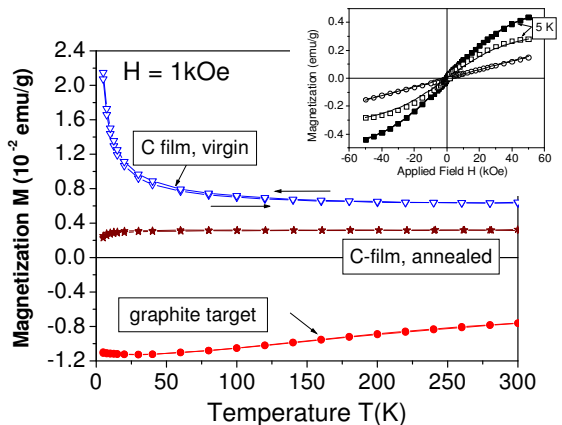


Fig. 1. Temperature dependence of the magnetization at 1 kOe obtained for the graphite target made from an ultra pure graphite powder [9] and the films, before and after annealing at 1000 °C for 10 h in vacuum. Inset: Field dependence of the magnetization of the carbon films at 5 K (■), and after subtraction of the Pauli-like term (□) given by the straight line through the points (○) $M = 3.1 \times 10^{-6} H$ emu/gOe. In the scale of the figure the Pauli-like magnetization curves measured at 300 K (before and after annealing) and at 5 K (after annealing) (○) practically coincide. The continuous lines through the points (■, □) are fits to the Langevin expression. Adapted from [10].

scribed by the usual Langevin expression from which we obtain a spin density $N_s \sim 10^{19} \text{ g}^{-1}$. According to earlier work [11] the localized spins in disordered carbon originate from unpaired electrons associated to the existence of broken σ -dangling bonds. Interestingly, the density of paramagnetic centers was correlated with the hydrogen concentration in earlier work (see [11] and Refs. therein). Annealing the disordered carbon material at 1000 °C for 10 h in vacuum reduces clearly the temperature dependent paramagnetic part, see Fig. 1. The observed behavior with annealing is not in favour of a magnetic impurity contribution.

Within experimental error the hysteresis loops for the disordered carbon films above 5 K are reversible. This indicates that a disordered mixture of sp^2 - sp^3 bonds, which exists in the disordered carbon films, does not trigger automatically ferromagnetism. The overall behavior as well as the spin density obtained for the disordered films prepared by PLD are very similar to those obtained for activated carbon fibers [12], results interpreted in terms of antiferromagnetically interacting spins from π -electrons originated at the edges of nanographite layers. One may doubt, however, on the existence of edge states of graphene layers in disordered carbon films. We note, however, that amorphous-like carbon prepared from targets with a large hydrogen/carbon ratio was reported to be ferromagnetic with a magnetization at saturation as large as 2 emu/g

at room temperature [13].

4. Ferromagnetism in carbon-based structures

There is a relatively large list of reports on organic ferromagnets since in 1991 two metal-ion free compounds with Curie temperatures of 0.65 K [14] and 16 K [15] were discovered. However, the research on the possible magnetic order in carbon-based structures appears to be older; for a recent review on magnetism in carbon-based materials in which most of the old work is included as well as a list of recent references on organic magnets, see [16]. In this contribution we would like to point out a few experimental facts that indicate the intrinsic, impurity free origin of the ferromagnetism in carbon structures with a Curie temperature above room temperature.

4.1. Impurity measurements

A systematic and full characterization of the magnetic impurity content in each of the samples is of primary importance and absolutely necessary. Part of the reason for the weak interest attracted by the ferromagneticlike hysteresis loops found in HOPG samples [17] as well as by older publications on magnetic carbon is probably due to unclear impurity characterization. To improve this situation radically we have used the method of “Particle Induced X-ray Emission” (PIXE) for the impurity characterization. Having a carbon matrix, this method reaches a sensitivity of ~ 0.1 ppm for all magnetic metallic impurities and therefore is very convenient for all relevant impurity analysis, prior and after any further characterization with MFM and SQUID and sample handling. The accelerator LIPSION in Leipzig with a proton micro-beam of 2.25 MeV energy and a broad-beam (~ 0.8 mm diameter) of 2.0 MeV energy are used for the

PIXE measurements. It allows simultaneously proton irradiation and element analysis (using the same protons). In comparison with the broad-beam, the micro-beam has the advantage that enables us to make a detailed element map of the sample within a depth of ~ 46 μm and check for inhomogeneous distributions of impurities. Typical spectra and element maps obtained in HOPG and fullerene samples as well as further details on the used nuclear nanoprobe method can be found in [19,20,21].

4.2. Ferromagnetic and paramagnetic signals in highly oriented pyrolytic graphite

For applied fields parallel to the graphene planes one is able to measure ferro- and/or paramagnetic signals

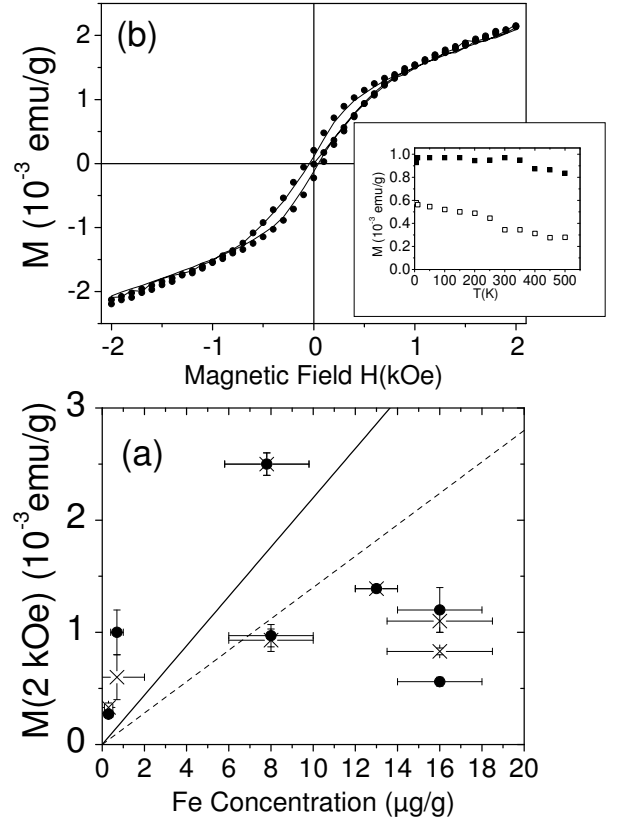


Fig. 2. (a) Magnetization at 2 kOe as a function of Fe concentration at two temperatures ((X): 300 K, (●): 5 K) for different HOPG and Kish graphite samples. The solid line represents the expected magnetization if Fe contained in the samples was in a ferromagnetic state. The dashed line represents the analogous relation for Fe_3O_4 . (b) Hysteresis loops at 5 K (●) and 300 K (continuous line) of a HOPG sample (FWHM $\sim 1.3^\circ$) for fields applied parallel to the graphene planes. No background was subtracted from the data. The inset shows the T -dependence of the magnetization at saturation (■) and its remanence (□) after annealing 16 h at 700 K. Adapted from [18].

in HOPG samples. Usually those signals would be overwhelmed by the diamagnetic one in the other field direction. In Ref. [18] we have studied in detail several HOPG samples from different sources with concentration of Fe-impurities between $< 0.3 \mu\text{g/g}$ to $\sim 19 \mu\text{g/g}$. We note that in those samples Fe is the main magnetic impurity (other magnetic metallic impurities are below $2 \mu\text{g/g}$). Figure 2(a) shows that the magnetization at 2 kOe, after subtraction of background contributions, does not show a correlation with the Fe-concentration. The results also indicate that the ferromagnetic like hysteresis loops are weakly temperature dependent between 5 K and 300 K, see inset in (b). A

naive estimate assuming that the Fe concentration behaves as Fe- or Fe_3O_4 -bulk in the carbon matrix would give the two lines shown in Fig. 2(a). Except for three HOPG samples the other show magnetization values below the ones expected from those Fe-lines. This figure clearly shows how small the ferromagnetic signals are that we are working with, as well as how much care is needed for the sample handling in all these studies. However, the assumption that such a small amount of Fe distributed in the carbon matrix behaves ferromagnetically is neither consistent with the behavior we observed in graphite samples with much larger Fe concentrations [18], nor with the recently obtained T -dependent, paramagnetic behavior in Fe irradiated graphite [23] nor in, e.g., $4d-5d$ metals, where paramagnetism as well as spin glass behaviors are measured for Fe concentrations of ~ 100 ppm or larger [22].

Figure 2(b) shows two hysteresis loops for a HOPG sample. We note that in this field range no sign of diamagnetism is measured but a paramagnetic behavior added to the hysteresis. This is one of some fortuitous cases where the diamagnetic component is small enough due to the small misalignment of the sample in the SQUID. The observed behavior in Fig. 2 is in clear contrast with the T -dependent paramagnetic contribution measured in samples with a larger amount of Fe-impurities [18,23]. The reason for the temperature independent (between 5 and 300 K) Pauli-like paramagnetism is probably related to the intrinsic lattice disorder as in disordered carbon samples (see Fig. 1). The results shown in Fig. 2 belong to a relatively disordered HOPG sample with $\text{FWHM} \simeq 1.3^\circ$ and a Pauli-like susceptibility $\chi \sim 5 \times 10^{-7}$ emu/gOe, smaller than that obtained for disordered carbon $\chi \sim 3 \times 10^{-6}$ emu/gOe [10]. We expect that by increasing the lattice disorder a Curie-like paramagnetic contribution will appear.

The overall results including those discussed in Sec. 4.4 suggest that special lattice disorder *and* the influence of a light atom like hydrogen may be the origin for the observed ferromagnetism. Recent density functional calculations indicate that H adsorption on vacancy dangling bonds gives rise to a localized magnetic moment of the order of $2.3\mu_B$ [24]. If these defects or just H-atoms at edge states can spin polarize the flat bands of graphite [25], then not Fe but a few tens of ppm H might be enough to trigger the magnetic order we observe. We stress that the ferromagnetic-like signal as well as the paramagnetism observed in HOPG are sample dependent. We expect that rather perfect samples annealed at high enough temperatures ($T \gtrsim 2500^\circ\text{C}$) and cooled down in high vacuum should show weaker ferro- and/or paramagnetic signals. Measurements on pure, specially annealed graphite powder [9] support this expectation.

4.3. Ferromagnetism in fullerenes

A magnetically ordered phase below the Curie temperature $T_C = 16$ K was discovered in the organic charge-transfer salt $[\text{TDAE}]\text{C}_{60}$ (TDAE = tetrakis(dimethylamino)ethylene) [15]. Afterwards, ferromagnetism was induced in C_{60} by photo-assisted oxidation, which remains up to $T_C \simeq 800$ K [26], results that were confirmed by another group [27]. Recently, ferromagnetic ordering in a hydrofullerite $\text{C}_{60}\text{H}_{24}$ with $T_C > 300$ K has been found [28]. Polymerization of C_{60} at temperatures and pressures near the cage collapse and graphitization of the anisotropic 2D rhombohedral Rh- C_{60} phase leads to ferromagnetism with $T_C \gtrsim 500$ K [29,30,31]. In general, the total concentration of magnetic impurities reported in those studies appears to be too low to give rise to the observed magnetization. Nevertheless, we need further evidence that supports a magnetic impurity independent ordering. We note that in $\text{C}_{60}\text{H}_{24}$ the initial ferromagnetic state strongly weakens after one year of storage, a result unlikely to come from magnetic impurities [28]. Measurements done on different polymerized samples with different Fe-concentration (up to $400 \mu\text{g/g}$) show very similar magnetization behavior (magnetization at saturation $M_s \simeq 150$ A/m = 0.065 emu/g). This fact as well as the influence of heat treatment on the magnetic behavior [32] do not favour an interpretation in terms of magnetic impurities. Furthermore, the small variation of remanence and coercivity with temperature gives no indication for magnetism of small particles, a behavior similar to that observed in different magnetic carbon-based structures including HOPG.

Magnetic force microscopy measurements performed in two polymerized fullerenes could resolve well defined magnetic domains [33]. These magnetic domains were obtained in a region where the magnetic impurity concentration was less than $1 \mu\text{g/g}$ as characterized by PIXE measurements [33,19]. These studies also showed that only $\sim 30\%$ of the pure sample area was magnetic, a result that speaks for the inhomogeneous character of the ferromagnetism and against a strong correlation between the magnetic ordering and rhombohedral structure. Recently published band structure calculations of Rh- C_{60} performed in the local-spin-density approximation found no magnetic solution for Rh- C_{60} and energy bands with different spins are found to be identical and not split, concluding that the rhombohedral distortion of C_{60} itself cannot induce magnetic ordering in polymerized fullerene [34]. These results are in agreement with the inhomogeneous magnetic distribution measured by MFM and suggest that the magnetic ordering is related to other carbon structures that are formed before the fullerene cages collapse [30]. New

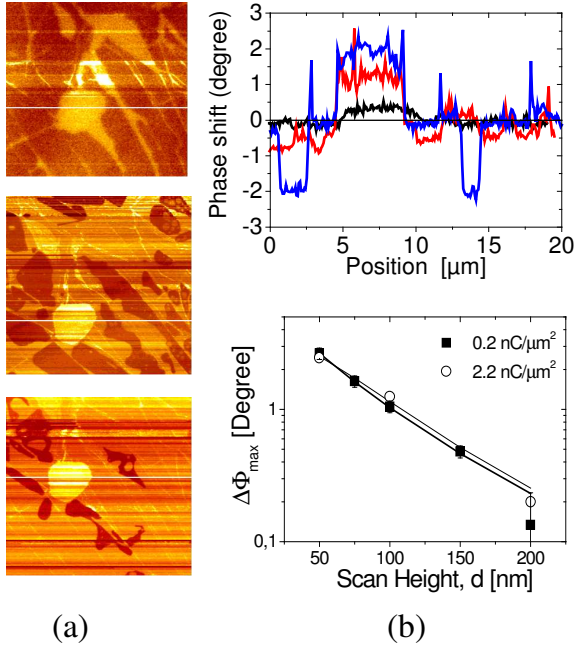


Fig. 3. (a) Magnetic force gradient images ($20 \times 20 \mu\text{m}^2$) of a spot and its surroundings irradiated with $0.115 \text{ nC}/\mu\text{m}^2$ (proton current $I = 171 \text{ pA}$). The images were taken, from top to bottom, before field application, after applying a field of $\sim 1 \text{ kOe}$ in the $+z$ direction parallel to the c -axis, and in the $-z$ direction. The tip-to-sample distance was 50 nm . (b) Top: The corresponding phase shift obtained at the line scans (white straight lines in figures (a)). The spot is located between $\sim 5 \mu\text{m}$ and $\sim 10 \mu\text{m}$ and the bottom, upper and middle lines in this region correspond to measurements before and after application of a field in $-z$ and $+z$ direction. Adapted from Ref. [37]. Bottom: Scanning height dependence of the maximum phase shift at proton irradiated spots with fluences of $0.2 \text{ nC}/\mu\text{m}^2$ and $2.2 \text{ nC}/\mu\text{m}^2$. Solid lines are fits with the point probe approximations. Adapted from Ref. [38].

theoretical and experimental work [35] suggest that hydrogen may play an important role on the magnetic ordering found in fullerenes and is something that one should carefully check in future studies, as the experiments described below indicate.

4.4. Magnetic ordering induced by proton irradiation

Proton irradiation of graphite provides us with the unique possibility of a complete analysis of the main magnetic elements in the sample and simultaneously implant hydrogen and produce defects that may trigger magnetic ordering in carbon structures. The measurements with the SQUID and the MFM we have done show indeed clear signs of magnetic ordering after irradiating HOPG samples [36,37] and disordered

carbon films [20]. In the published literature on magnetism in carbon-based structures one realizes that apparently hydrogen (or maybe also other light atoms like oxygen) plays a role in the reported ferromagnetism. Specially the work in Ref. [13] showed clearly that the saturation magnetization of disordered carbon prepared from different H-rich targets increases with the H-concentration of the starting materials.

The results after proton irradiation leave no doubt that magnetic ordering exists in a carbon structure without the influence of magnetic ions. Neither the total amount of magnetic impurities is sufficient to account for the measured magnetization nor the creation of magnetic spots in the micrometer range with the proton micro-beam can be understood based on magnetic metal-ion impurity concentration below 1 ppm as the PIXE results indicate. An example of a magnetic spot and the field gradient response after applying a magnetic field in different directions is shown in Fig. 3. We can clearly recognize the magnetic signal at the bombardment position as well as magnetic “structures” outside the spot, which also change after application of an external magnetic field (note that the MFM measurements were always done without applied field) [37]. In the figure we show also how the magnetic signal depends on the sample-tip height of the MFM. Using these data and different models from literature we can estimate, although with a relatively large error, a magnetization at the spot surface of the order of $\sim 10^6 \text{ A/m} \sim 400 \text{ emu/g}$ [38].

5. Open questions

Further experimental characterization (using the broad spectrum of methods in magnetism research) and sample preparation studies are necessary to understand and stabilize the magnetic ordering found in carbon structures. The following questions are a short list that should be clarified in the near future:

- (i) The role of H-atoms, implanted by irradiation as well as those already in the sample.
- (ii) The contribution to the magnetic ordering from lattice defects produced by irradiation and their possible influence as H-trapping centers.
- (iii) The effective magnetic moment of magnetic impurities in graphite as well as in disordered carbon structures.
- (iv) The maximum achievable saturation magnetization in carbon structures. According to theoretical work this might be as large as three times that of pure Fe [39].
- (v) The range of Curie temperature.

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